特7

(19)日本国特許庁（ＪＰ）　(12) **特　許　公　報**（Ｂ２）　(11)特許番号

第2941848号

(45)発行日　平成11年(1999) 8月30日　(24)登録日　平成11年(1999) 6月18日

(51)Int.Cl.⁶	識別記号	ＦＩ		
Ｂ４１Ｍ　5/26		Ｂ４１Ｍ　5/26		Ｘ
Ｇ１１Ｂ　7/24	５１１	Ｇ１１Ｂ　7/24		５１１

請求項の数２（全 ４ 頁）

(21)出願番号　特願平1－178938

(22)出願日　平成１年(1989) 7月13日

(65)公開番号　特開平3－231889

(43)公開日　平成３年(1991) 10月15日

審査請求日　平成８年(1996) 6月20日

(31)優先権主張番号　特願昭63－179186

(32)優先日　昭63(1988) 7月20日

(33)優先権主張国　日本（ＪＰ）

(31)優先権主張番号　特願平1－70585

(32)優先日　平１(1989) 3月24日

(33)優先権主張国　日本（ＪＰ）

(31)優先権主張番号　特願平1－142086

(32)優先日　平１(1989) 6月6日

(33)優先権主張国　日本（ＪＰ）

(73)特許権者　999999999
株式会社リコー
東京都大田区中馬込１丁目３番６号

(72)発明者　針谷　真人
東京都大田区中馬込１丁目３番６号　株式会社リコー内

(72)発明者　井手　由紀雄
東京都大田区中馬込１丁目３番６号　株式会社リコー内

(72)発明者　山田　勝幸
東京都大田区中馬込１丁目３番６号　株式会社リコー内

(74)代理人　弁理士　小松　秀岳　（外２名）

審査官　秋山　祐子

最終頁に続く

(54)【発明の名称】　光記録媒体

(57)【特許請求の範囲】

【請求項１】基板上に下記一般式で示され、かつ４～６元化合物から成り、その構造がカルコパイライト型構造である記録層を有することを特徴とする相変化型光記録媒体。

一般式　$X \cdot Y \cdot Z_2$

但し、ＸはAg、Zn、Cdから選ばれた一種以上二種までの元素。

ＹはAl、Ga、In、Si、Snから選ばれた一種以上二種までの元素

ＺはSb、Bi、Ｐ、Teから選ばれた一種以上二種までの元素。

（但し、一般式$X \cdot Y \cdot Z_2$で、$AgInTe_2$、$AgGaTe_2$、$AgAlTe_2$は含まない。）

【請求項２】記録層を構成する元素の組み合わせによるカルコパイライト型化合物が下記一般式の何れかで示されることを特徴とする請求項（１）記載の相変化型光記録媒体。

・４元素一般式

1. $(Ag_{1-x} \cdot II_x) \cdot III \cdot Te_2$
2. $(Ag_{1-x} \cdot II_x) \cdot IV \cdot V_2$
3. $II \cdot (III_{1-y} \cdot IV_y) \cdot V_2$
4. $Ag \cdot III \cdot (V_{1-z} \cdot Te_z)_2$
5. $II \cdot IV \cdot (V_{1-z} \cdot Te_z)_2$

・５元素一般式

1. $(Zn_{1-x} \cdot Cd_x) \cdot (Si_{1-y} \cdot Sn_y) \cdot V_2$
2. $(Zn_{1-x} \cdot Cd_x) \cdot IV \cdot (V_{1-z} \cdot V'_{1-z})_2$
3. $II \cdot (Si_{1-y} \cdot Sn_y) \cdot (V_{1-z} \cdot V'_z)_2$
4. $(Ag_{1-x} \cdot II_x) \cdot (III_{1-y} \cdot III'_y) \cdot Te_2$
5. $(Ag_{1-x} \cdot II_x) \cdot (III_{1-y} \cdot IV_y) \cdot Te_2$

6. $(Ag_{1-x}\cdot II_x)\cdot(Si_{1-y}\cdot Sn_y)\cdot V_2$
7. $II\cdot(III_{1-y}\cdot IV_y)\cdot(V_{1-z}\cdot V'_z)_2$
8. $II\cdot(III_{1-y}\cdot IV_y)\cdot(V_{1-z}\cdot Te_z)_2$

・６元系一般式

1. $(Zn_{1-x}\cdot Cd_x)\cdot(Si_{1-y}\cdot Sn_y)\cdot(V_{1-z}\cdot V'_z)_2$
2. $(Ag_{1-x}\cdot II_x)\cdot(Si_{1-y}\cdot Sn_y)\cdot(V_{1-z}\cdot V'_z)_2$
3. $(Zn_{1-x}\cdot Cd_x)\cdot(III_{1-y}\cdot IV_y)\cdot(V_{1-z}\cdot V'_z)_2$
4. $(Zn_{1-x}\cdot Cd_x)\cdot(Si_{1-y}\cdot Sn_y)\cdot(V_{1-z}\cdot Te_z)_2$
5. $(Zn_{1-x}\cdot Cd_x)\cdot(III_{1-y}\cdot IV_y)\cdot V_{1-z}\cdot Te_z)_2$
6. $(Ag_{1-x}\cdot II_x)\cdot(III_{1-y}\cdot IV_y)\cdot(V_{1-z}\cdot Te_z)_2$

但し、

上記一般式のII、II_xはII b族元素のZn又はCdを表す。

III、III_{1-y}は同じくIII b族元素のAl又はGa又はInを表し、III_{1-y}とIII'_yは互いに異なるIII b族元素を表す。

IV、IV_yは同じくIV b族元素のSi又はSnを表す。

V、V_{1-z}は同じくV b族元素のSb又はBi又はPを表し、V_{1-z}とV'_zは互いに異なるV b族元素を表す。

又、$0<x<1$、$0<y<1$、$0<z<1$である。

【発明の詳細な説明】

［産業上の利用分野］

本発明は光による記録層の相変化を利用して情報の記録再生及び書き換えを行うための相変化型光情報媒体に関する。

［従来の技術］

電磁波特にレーザービームの照射により情報の記録・再生および消去可能な光メモリー媒体の一つとして、結晶－非晶質相間或いは結晶－結晶相間の転移を利用する、いわゆる相変化型記録媒体が良く知られている。特に光磁器メモリーでは困難な単一ビームによるオーバーライトが可能であり、ドライブ側の光学系も、より単純であることなどから最近その研究開発が活発になっている。電子通信学会論文集CPM87－90、その代表的な材料例として、USP3,530,441に開示されているようにGe－Te、Ge－Te－Sb、Ge－Te－S、Ge－Se－S、Ge－Se－Sb、Ge－As－Se、In－Te、Se－Te、Se－As等所謂カルコゲン系合金材料が挙げられる。又、安定性、高速結晶化等の向上を目的にGe－Te系にAu（特開昭61－219692）、Sn及びAu（特開昭61－270190）、Pd（特開昭62－19490）等を添加した材料の提案や、記録／消去の繰返し性能向上を目的にGe－Te－Se－Sbの組成比を特定した材料（特開昭62－73438）の提案等もなされている。

しかし、そのいずれも相変化型書換え可能光メモリー媒体として要求された諸特性のすべてを満足し得るものとはいえない。特に記録感度、消去感度の向上、オーバーライト時の消し残りによる消去比低下の防止、並びに記録部、未記録部の長寿命化が解決すべき最重要課題となっている。

［発明が解決しようとする課題］

本発明は従来技術における上記問題点を解消し高速消去、記録感度、消去感度の向上、記録部の安定性等の特性を全て満足する新規な相転移性多元化合物を用いたオーバーライト可能な相変化型情報記録媒体を提供しようとするものである。

［課題を解決するための手段］

上記課題を解決するための本発明の構成は、基板上に下記一般式で示され、かつ４～６元化合物から成り、その構造がカルコパイライト型構造である記録層を有する相変化型記録媒体。

一般式　$X\cdot Y\cdot Z_2$

但し、

XはAg、Zn、Cdから選ばれた一種以上二種までの元素、

YはAl、Ga、In、Si、Snから選ばれた一種以上二種までの元素、

ZはSb、Bi、P、Teから選ばれた一種以上二種までの元素、

（但し、一般式$X\cdot Y\cdot Z_2$で、$AgInTe_2$、$AgGaTe_2$、$AgAlTe_2$は含まない。）

を表し、上記一般式の構成元素は４元素から最高６元素までである。

そしてこの様な多元化合物としての元素の組合わせは以下の一般式で示される。

・４元系一般式

1. $(Ag_{1-x}\cdot II_x)\cdot III\cdot Te_2$
2. $(Ag_{1-x}\cdot II_x)\cdot IV\cdot V_2$
3. $II\cdot(III_{1-y}\cdot IV_y)\cdot V_2$
4. $Ag\cdot III\cdot(V_{1-z}\cdot Te_z)_2$
5. $II\cdot IV\cdot(V_{1-z}\cdot Te_z)_2$

・５元素一般式

1. $(Zn_{1-x}\cdot Cd_x)\cdot(Si_{1-y}\cdot Sn_y)\cdot V_2$
2. $(Zn_{1-x}\cdot Cd_x)\cdot IV\cdot(V_{1-z}\cdot V'_{1-z})_2$
3. $II\cdot(Si_{1-y}\cdot Sn_y)\cdot(V_{1-z}\cdot V'_z)_2$
4. $(Ag_{1-x}\cdot II_x)\cdot(III_{1-y}\cdot III'_y)\cdot Te_2$
5. $(Ag_{1-x}\cdot II_x)\cdot(III_{1-y}\cdot IV_y)\cdot Te_2$
6. $(Ag_{1-x}\cdot II_x)\cdot(Si_{1-y}\cdot Sn_y)\cdot V_2$
7. $II\cdot(III_{1-y}\cdot IV_y)\cdot(V_{1-z}\cdot V'_z)_2$
8. $II\cdot(III_{1-y}\cdot IV_y)\cdot(V_{1-z}\cdot Te_z)_2$

・６元系一般式

1. $(Zn_{1-x}\cdot Cd_x)\cdot(Si_{1-y}\cdot Sn_y)\cdot(V_{1-z}\cdot V'_z)_2$
2. $(Ag_{1-x}\cdot II_x)\cdot(Si_{1-y}\cdot Sn_y)\cdot(V_{1-z}\cdot V'_z)_2$
3. $(Zn_{1-x}\cdot Cd_x)\cdot(III_{1-y}\cdot IV_y)\cdot(V_{1-z}\cdot V'_z)_2$
4. $(Zn_{1-x}\cdot Cd_x)\cdot(Si_{1-y}\cdot Sn_y)\cdot(V_{1-z}\cdot Te_z)_2$
5. $(Zn_{1-x}\cdot Cd_x)\cdot(III_{1-y}\cdot IV_y)\cdot V_{1-z}\cdot Te_z)_2$

6. $(Ag_{1-x} \cdot II_x) \cdot (III_{1-y} \cdot IV_y) \cdot (V_{1-z} \cdot Te_z)_2$
但し、
上記一般式のII、II_xはII b族元素のZn又はCdを表す。
III、III_{1-y}は同じくIII b族元素のAl又はGa又はInを表し、III_{1-y}とIII'_yは互いに異なるIII b族元素を表す。
IV、IV_yは同じくIV b族元素のSi又はSnを表す。
V、V_{1-z}は同じくV b族元素のSb又はBi又はPを表し、V_{1-z}とV'_zは互いに異なるV b族元素を表す。
又、$0<x<1$、$0<y<1$、$0<z<1$である。
又、上記一般式で示される化合物の構造はカルコパライト型もしくは、これに類似した構造を持つものである。類似した構造とは、例えばカルコパイライト構造において、その陽イオンの存在すべき位置の格子点がVacancyで置きかえられた構造を有するものとか、２種の陽イオンのカルコパイライト構造における規則的配置が消失したもの等である。

又さらに上記一般式で表わされる多元化合物にVII b族の元素を添加することができる。

カルコパイライト構造を有する化合物は一般にI b−III b−VI b_2、II b−IV b−V b_2の形で表わされる。

結晶系は一般に正方晶であり光学的異方性が認められ、これらの性質を効果的に利用できる。即ち多元系（４元〜６元）にした場合においても請求項２に記載の一般式をとる形の化合物であれば、カルコパイライトもしくはこれに類似した構造をとることが期待できることと、多元系化合物（４元〜６元）としての物性の拡大が望める。

すなわち、本発明は上記多元化合物よりなる記録層を設けたことを特徴とするものである。

本発明の記録層に用いられる前記一般式の多元化合物はX、又はY、又はZの各々の元素および元素比をかえることにより融点、バンドギャップ、熱伝導率、比熱、結晶化温度、活性化エネルギー、及びその光学定数等を任意に変化させることが可能である。すなわち本発明の基礎をなすI b III b VI b_2化合物、あるいはII b IV b V b_2化合物は融点が約400〜800℃前後にあるものが多く、又、そのエネルギーギャップも現在多く使用されている（GaAl）As系の半導体レーザに対して効率的に吸収可能な範囲にあるため、感度の向上及び高速消去が期待できる。

本発明はこれら三元系化学物の有する各種物性の幅を多元素系とすることにより大きく拡大することが期待できるため現在相変化型光記録媒体が有する前記問題点を解消することが可能となる。

又前記一般式の化合物の場合、成膜条件によっては従来の非晶質−結晶質間の相転移と同時に結晶質−結晶質間の相転移も可能である。

以上のような本発明の新規な相転移性多元化合物の具体的な例としては、

$(Zn_{1-x}Cd_x)Sn(Sb_{1-z}P_z)_2$、
$(Ag_{1-x}Zn_x)(In_{1-y}Ga_y)Te_2$、
$Zn(In_{1-y}Sn_y)(Sb_{1-z}P_z)_2$、
$(Zn_{1-x}Cd_x)(In_{1-y}Sn_y)(Sb_{1-z}P_z)_2$、
$(Zn_{1-x}Cd_x)(In_{1-y}Sn_y)(Sb_{1-z}Te_z)_2$、
$(Ag_{1-x}Zn_x)(In_{1-y}Sn_y)(Sb_{1-z}Te_z)_2$等が挙げられる。

そしてさらに感度の向上、高速記録、高速消去を行うため、添加物としてVII b族元素を添加することができる。

例えばその様な記録材として
$Ag(In_{1-x}Sb_x)Te_2 \cdot Cl$等があげられる。

基板としてはガラス、ポリメチルメタクリレート、ポリカーボネート等が使用される。

本発明の光情報記録媒体を作るには所定の組成比のターゲットを作製し、スパッター法による方法が好適である。又膜の組成ずれを補正するために必要に応じて単元素のチップを用いる場合もある。

こうして形成された記録層の厚さは通常100〜1500Å、好ましくは200〜1000Åであるが、基板および保護層等の光学特性を考慮した上で最適膜厚を設計する必要がある。なお記録層を比晶質状態にするか、或いは結晶状態にするかは蒸着時の基板温度によって決定され、常温の場合は非晶質状態となる。又必要に応じて基板温度をあげることあるいはアニールをほどこすことにより結晶状態にすることもできる。

本発明では記録層上に更に保護層を設けることができる。保護層の材料としては熱的に安定な窒化ケイ素、窒化アルミニウム等の窒化物；二酸化ケイ素、二酸化チタン等の酸化物等が使用される。なお保護層の厚さは通常300〜1500Å好ましくは、約1000Åであるが基板、記録の光学特性を考慮した上で設計する必要がある。形成法は記録層の場合と同様、通常スパッタ法が適用される。

［実施例］

以下に本発明を実施例によって更に詳しく説明する。

実施例１

$(Ag_{0.5}Zn_{0.5})(In_{0.5}Sn_{0.5})(Sb_{0.5}Te_{0.5})_2$の組成を有するスパッタ用ターゲットを作製し、直径130mm、厚さ1.2mmのガラス基板上に実施例１、２と同じ方法により1000Å厚の記録層を設けた後、窒化シリコンを保護膜として1000Å厚形成した。そして初めにテストピースにより本記録層の光学特性及び熱特性を実施例１、２、３と同じく分光光度計及びDSCにより測定した。反射率変化は蒸着後（非晶質）と初期化後（結晶質）（λ＝780nm）で20％程度であった。又透過率は〜15％程度であり、単独の$AgInTe_2$より20％程小さく、又同じく単独の$ZnSnSb_2$より10％程大きい。従って吸収効率の増大と共に干渉によるコントラストの増大が可能となる。又融点は490℃、結晶化温度は〜150℃前後であった。

次に本記録層のディスク特性を実施例１、２と同様に測定した。先ず記録媒体を1800rpmの速度で回転させながらビーム径を１μｍφ程度に絞った半導体レーザ光（λ＝780nm）を照射することにより、記録、再生及び消去を行った。なお記録出力は記録最小パワー8mW、再生出力2mW消去出力は消去最小パワー5mWであった。又この出力／消去条件3MHzで記録後さらに2MHzでオーバーライトの実験を行った。

その結果初期記録のC/N比51dB、オーバーライト後も49dBであった。一方この時の消去率は30dBであった。

又10,000回の記録、消去の繰返し実験を行ったが、信号レベルの低下はほとんど認められなかった。

実施例２

（$Zn_{15}Cd_{10}$）Sn_{25}（$Sb_{30}P_{20}$）の組成を有するスパッタ用８ターゲットを作製し、実施例１と同じ方法で記録層を形成し、同じ方法で性質を測定した。

本記録層の融点は～510℃であり、結晶化温度は～150℃前後であった。又非晶質と初期化後（結果化）の間の反射率変化は18％程度であった（測定波長780nm）。

これらの値はZn、Cd、Sb、Ｐの組成比をかえることによって変化することはもちろんである。このことは目的に応じて記録感度、消去感度及び記録の長寿命化をはかる為の自由度が広いことを示している。即ち、$ZnSnSb_2$、$CdSnP_2$化合物の各々の有する特性（融点、干渉効果等）をうまく組み合せる事により感度及びコントラストの向上をはかる事ができる。

次に初期化後の記録媒体を1800rpmの速度で回転させながらビーム径を１μｍφ程度に絞った半導体レーザー光（発振波長λ＝780nm）の照射することにより、記録、再生及び消去を行った。

なお、記録出力は記録最小パワー8mW、再生出力は2mW、消去出力、消去最小パワーは5mWである。又この出力／消去条件で記録後、さらに2M Hzでオーバーライト試験を行った。

その結果、初期記録のC/N比は51dBでオーバーライト後も50dBと殆ど変らなかった。又この時の消去率は31dBであり消去残りが若干認められるが、充分使用可能な段階であることが確認された。又10,000回の記録、消去のくり返し実験を行ったが、信号レベルの低下はほとんど＊＊認められず、くり返し特性も良好であることが確認された。

実施例３

Zn_{25}（$In_{10}Sn_{15}$）（Sb_{50}）の組成を有するターゲットを作製し、実施例１と同じ方法で光情報記録媒体を作製した。テストピースにより光学特性、熱特性をそれぞれ分光光度径及びDSCにより測定した。反射率変化は蒸着後（非晶質）と初期化後（結晶質）（λ＝780nm）で18％程度であり、融点は～430℃、結晶化温度は～135℃前後であった。本実施例で用いた記録材料の特徴はカルコパイライト化合物で融点が最も低い$ZnSnSb_2$を用いて融点を下げ、さらInの効果でバンドギャップを広げて干渉効果を利用する事によコントラストの向上をはかる事にある。

次に初期化後の記録媒体を1800rpmの速度で回転させながらビーム径を１μｍφ程度に絞った半導体レーザー光（λ＝780）を照射することにより記録、再生及び消去をおこなった。なお記録出力は記録最小パワー7mW、再生出力2mW、消去出力最小パワーは5mWであった。又この出力／消去条件で記録後さらにに2MHzでオーバーライト実験を行った。

その結果初期記録のC/N比は52dB、オーバーライト後も50dBと良好な値を示した。又この時の消去率は30dBであった。

又10,000回の記録、消去のくり返し実験を行ったが、信号レベルの低下はほとんど認められなかった。

以上の実施例から本発明の記録層を用いることにより、記録感度、消去感度及び消去率の向上ならびにくり返し特性の改良が実現できることが明らかである。

［発明の効果］

以上説明したように、本発明で用いられる前記一般式の多元化合物は、その構成元素比を変化させることにより、その光学定数をはじめ、バンドギャップ、熱伝導率、比熱、融点、結晶化点及び活性化エネルギーを広い範囲で任意に制御することが可能なため相変化型光メモリー用記録材料として使用した時、記録感度、消去感度の向上、及び消去の改良そして記録の長寿命化をはかることができる。

フロントページの続き

(72)発明者　岩崎　博子
東京都大田区中馬込１丁目３番６号　株式会社リコー内

(56)参考文献　特開　昭64－10439（ＪＰ，Ａ）
特開　平１－94545（ＪＰ，Ａ）

(58)調査した分野(Int.Cl.^{6}，ＤＢ名)
B41M　5/26

PATENT ABSTRACTS OF JAPAN

(11)Publication number : 03-231889
(43)Date of publication of application : 15.10.1991

(51)Int.Cl. B41M 5/26
G03C 1/705
G11B 7/24

(21)Application number : 01-178938
(22)Date of filing : 13.07.1989

(71)Applicant : RICOH CO LTD
(72)Inventor : HARIGAI MASATO
IDE YUKIO
YAMADA KATSUYUKI
IWASAKI HIROKO

(30)Priority

Priority number : 63179186 Priority date : 20.07.1988 Priority country : JP
64 70585 24.03.1989 JP
01142086 06.06.1989 JP

(54) OPTICAL RECORDING MEDIUM

(57)Abstract:
PURPOSE: To improve recording sensitivity and erasure sensitivity by forming an optical recording medium by providing a recording layer having a chalcopyrite structure composed of a 4-6-element type compound represented by a specific general formula on a substrate.
CONSTITUTION: A target having a composition ratio represented by formula I (wherein X is an element of the Groups Ib, IIb of the Periodic Table, Y is an element of the Groups IIIb, IVb, Vb of the Periodic Table and Z is an element of the Groups Vb, VIb of the Periodic) is prepared. A sputtering method is adapted to this target to form a recording layer having a chalcopyrite structure composed of the compound having the composition ratio represented by formula I on a substrate composed of glass or polycarbonate to obtain an optical recording medium. The thickness of the recording layer is pref. about 200-1,000Å and a protective layer based on a material such as thermally stable silicon nitride can be laminated to the recording layer.

$X \cdot Y \cdot Z_2$ I

LEGAL STATUS

[Date of request for examination]

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's decision of rejection]

[Date of requesting appeal against examiner's decision of rejection]

[Date of extinction of right]

* NOTICES *

CLAIMS

---

(57) [Claim(s)]
[Claim 1] The phase-change type optical recording medium characterized by being shown by the following general formula on a substrate, and for 4 to 6 yuan consisting of a compound, and having the record layer the structure of whose is KARUKO pyrite type structure.
General formula X-Y-Z2, however X are an element to two sorts more than a kind chosen from Ag, Zn, and Cd.
The element Z to two sorts is an element to two sorts more than a kind chosen from Sb, Bi, P, and Te more than a kind as which Y was chosen from aluminum, Ga, In, Si, and Sn.
(However, AgInTe2, AgGaTe2, and AgAlTe2 do not contain by general formula X-Y-Z2.)
[Claim 2] The phase-change type optical recording medium given in a claim (1) characterized by showing the KARUKO pyrite type compound by the combination of the element which constitutes a record layer depending on any of the following general formula they are.
- 4 element general formula 1. -III-Te22. (Ag1-x-IIx) -IV-V23.II- (Ag1-x-IIx) -V24.Ag-III- (III1-y-IVy) 25.II-IV- (V1-z-Tez) 2 and 5 element general formula 1. (V1-z-Tez) - (Zn1-x-Cdx) -V22. (Si1-y-Sny) - IV- (Zn1-x-Cdx) 23.II- (V1-z-V'1-z) - (Si1-y-Sny) 24. (V1-z-V'z) - (Ag1-x-IIx) -Te25. (III1-y-III'y) - (Ag1-x-IIx) -Te26. (III1-y-IVy) - (Ag1-x-IIx) -V27.II- (Si1-y-Sny) - (III1-y-IVy) 28.II- (V1-z-V'z) - (III1-y-IVy) 2.6 yuan system general formula 1. (V1-z-Tez) - (Zn1-x-Cdx) - (Si1-y-Sny) 22. (V1-z-V'z) - (Ag1-x-IIx) - (Si1-y-Sny) 23. (V1-z-V'z) - (Zn1-x-Cdx) - (III1-y-IVy) 24. (V1-z-V'z) (Zn1-x-Cdx) - (Si1-y-Sny) -(V1-z-Tez)25.(Zn1-x-Cdx) -(III1-y-IVy) -V1-z-Tez26.(Ag1-x-IIx) -(III1-y-IVy) -(V1-z-Tez) 2 -- however II of the above-mentioned general formula and IIx express Zn of a II b group element, or Cd.
Similarly III and III1-y expresses Al of a III b group element, Ga, or In, and III1-y and III'y express a mutually different III b group element.
Similarly IVIVy expresses Si or Sn of a IV b group element.
Similarly V and V1-z expresses Sb of a V b group element, Bi, or P, and V1-z and V'z express a mutually different V b group element.
Moreover, it is $0< x<1$, $0< y<1$, and $0< z<1$.

[Translation done.]

* NOTICES *

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[Industrial Application]
this invention relates to the phase-change type light information media for performing informational record reproduction and informational rewriting using the phase change of the record layer by light.
[Description of the Prior Art]
The so-called phase-change type record medium which uses transition between a crystal-amorphous interphase or a crystal-crystal phase by irradiation of an electromagnetic wave, especially a laser beam as one of the optical-memory media in which informational record and reproduction, and elimination are possible is known well. Especially, by optical porcelain memory, since over-writing by the difficult single beam is possible and the optical system by the side of a drive is also more simple, the research and development are active recently. As the Institute of Electronics and Communication Engineers collected works CPM 87-90 and its typical example of material, the so-called charges of a chalcogen system alloy, such as germanium-Te, germanium-Te-Sb, germanium-Te-S, germanium-Se-S, germanium-Se-Sb, germanium-As-Se, In-Te, Se-Te, and Se-As, are mentioned as indicated by USP3,530,441. Moreover, the proposal of the material which added Au (JP,61-219692,A), Sn, Au (JP,61-270190,A), Pd (JP,62-19490,A), etc. in the germanium-Te system for the purpose of the improvement in stability, high-speed crystallization, etc., the proposal of material (JP,62-73438,A) which specified the composition ratio of germanium-Te-Se-Sd for the purpose of the improvement in repeatability ability of record/elimination are made.
However, the neither can say it as what may satisfy many properties of all demanded as a phase-change type rewritable optical-memory medium. It is the problem of the utmost importance which should be erased at the time of improvement in record sensitivity and elimination sensitivity, and over-writing, and the reinforcement of prevention of the elimination ratio fall by the remainder and the Records Department, and the non-Records Department should solve especially.
[Problem(s) to be Solved by the Invention]
this invention tends to offer the phase-change type information record medium [over-write / record medium] using the new phase transition nature plural compounds with which the above-mentioned trouble in the conventional technology is canceled, and it is satisfied of all properties, such as improvement in high-speed elimination and record sensitivity and elimination sensitivity, and the stability of the Records Department.
[The means for solving a technical problem]
The composition of this invention for solving the above-mentioned technical problem is a phase-change type record medium which is shown by the following general formula on a substrate, and consists of a compound, and has the record layer the structure of whose is KARUKO pyrite type structure. [of 4 to 6 yuan]
general formula X-Y-Z2 however -- more than a kind as which X was chosen from Ag, Zn, and Cd -- element to two sorts more than a kind as which Y was chosen from aluminum, Ga, In, Si, and Sn -- element to two sorts more than a kind as which Z was chosen from Sb, Bi, P, and Te -- element

(however, it is general formula X-Y-Z2, and AgInTe2, AgGaTe2, and AgAlTe2 do not contain.) to two sorts
A ** table is carried out and the composition elements of the above-mentioned general formula are even a maximum of 6 elements from four elements.
And the combination of the element as such plural compounds is shown by the following general formulas.
- 4 yuan system general formula 1. -III-Te22. (Ag1-x-IIx) -IV-V23.II- (Ag1-x-IIx) -V24.Ag-III- (III1-y-IVy) 25.II-IV- (V1-z-Tez) 2 and 5 element general formula 1. (V1-z-Tez) - (Zn1-x-Cdx) -V22. (Si1-y-Sny) -IV- (Zn1-x-Cdx) 23.II- (V1-z-V'1-z) - (Si1-y-Sny) 24. (V1-z-V'z) - (Ag1-x-IIx) -Te25. (III1-y-III'y) - (Ag1-x-IIx) -Te26. (III1-y-IVy) - (Ag1-x-IIx) -V27.II- (Si1-y-Sny) - (III1-y-IVy) 28.II- (V1-z-V'z) - (III1-y-IVy) 2.6 yuan system general formula 1. (V1-z-Tez) - (Zn1-x-Cdx) - (Si1-y-Sny) 22. (V1-z-V'z) - (Ag1-x-IIx) - (Si1-y-Sny) 23. (V1-z-V'z) - (Zn1-x-Cdx) - (III1-y-IVy) 24. (V1-z-V'z) (Zn1-x-Cdx) -(Si1-y-Sny) -(V1-z-Tez)25.(Zn1-x-Cdx) -(III1-y-IVy) -V1-z-Tez26.(Ag1-x-IIx) -(III1-y-IVy) -(V1-z-Tez) 2 However II of the above-mentioned general formula and IIx are Zn of a II b group element, or Cd. It expresses.
Similarly III and III1-y expresses aluminum of a III b group element, Ga, or In, and III1-y and III'y express a mutually different III b group element.
Similarly IVIVy expresses Si or Sn of a IV b group element.
Similarly V and V1-z expresses Sb of a V b group element, Bi, or P, and V1-z and V'z express a mutually different V b group element.
Moreover, it is $0< x<1$, $0< y<1$, and $0< z<1$.
Moreover, the structure of the compound shown by the above-mentioned general formula has a KARUKO pearlite type or structure similar to this. Similar structures are what has the structure where the lattice point of the position where the cation should exist was replaced by Vacancy, the thing to which the regular arrangement in the KARUKO pyrite structure of two sorts of cations disappeared for example, in KARUKO pyrite structure.
Furthermore, a VII b group's element can be added to the plural compounds expressed with the above-mentioned general formula.
Generally the compound which has KARUKO pyrite structure is expressed with the form of I b-III b-VI b2 and II b-IV b-V b2.
Generally it is a tetragonal phase, an optical anisotropy is accepted, and crystal system can use these properties effectively. That is, if it is the compound of the form where a general formula according to claim 2 is taken when it is made plural systems (- of 4 yuan 6 yuan), expansion of the physical properties as a plural system compound (- of 4 yuan 6 yuan) can be wished that it is expectable to take structure similar to a KARUKO pyrite or this.
That is, this invention is characterized by preparing the record layer which consists of the above-mentioned plural compounds.
The plural compounds of the aforementioned general formula used for the record layer of this invention can change arbitrarily the melting point, a band gap, thermal conductivity, the specific heat, crystallization temperature, activation energy, its optical constant, etc. by changing the elements and element ratio of X, Y, or Z. That is, I b III b VI b2 compound which makes the foundation of this invention, or II b IV b V b2 compound has many which have the melting point around about 400-800 degrees C, and since the energy gap is also in the absorbable range efficiently to the semiconductor laser of As system used now (GaAl), it can expect improvement and high-speed elimination of sensitivity.
[many]
Since this invention can expect expanding greatly by making into a multi-element system width of face of the various physical properties which these ternary system chemistry object has, it becomes possible [canceling the aforementioned trouble which the present phase-change type optical recording medium has].
Moreover, in the case of the compound of the aforementioned general formula, simultaneously with the phase transition between the conventional amorphous-crystalline substances, depending on membrane

formation conditions, the phase transition between crystalline-substance-crystalline substances is also possible.
As the concrete example of the new phase transition nature plural compounds of the above this inventions Sn (Zn1-xCdx) 2, (Sb1-zPz) (Ag1-xZnx) Te2, Zn (In1-yGay) (In1-ySny) (Sb1-zPz) 2, 2 (Sb (In(Zn1-xCdx)1-ySny)1-zPz), 2 (Sb(In(Zn1-xCdx)1-ySny)1-zTez), and 2 (Sb(In(Ag1-xZnx)1-ySny)1-zTez) grades are mentioned.
And since improvement in sensitivity, high-speed record, and high-speed elimination are performed further, a VII b group element can be added as an additive.
For example, Ag(In1-xSbx) Te2, Cl, etc. are raised as such record material.
Glass, a polymethylmethacrylate, a polycarbonate, etc. are used as a substrate.
The target of a predetermined composition ratio is produced to make the optical information record medium of this invention and the method by the sputtering technique is suitable to make. The chip of a single element may be used for an amendment sake for a composition gap of **** if needed.
In this way, usually, although the formed record layer thickness is 200-1000A preferably, after taking into consideration optical properties, such as a substrate and a protective layer, it needs to design the 100-1500A of the optimal thickness. in addition, a record layer -- a ratio -- it will be determined by the substrate temperature at the time of vacuum evaporationo whether it changes into a crystalloid state or it is made a crystallized state, and, in the case of ordinary temperature, it will be in an amorphous state Moreover, it can also be made a crystallized state by giving raising substrate temperature if needed or annealing.
In this invention, a protective layer can be further prepared on a record layer. As a material of a protective layer, oxides, such as nitride; silicon dioxides, such as stable silicon nitride and alumimium nitride, and a titanium dioxide, etc. are used thermally. In addition, although it was about 1000A, after usually taking into consideration preferably the 300-1500A of substrates and the optical properties of record, it is necessary to design the thickness of a protective layer. A spatter is usually applied by the forming method like the case of a record layer.
[Example]
An example explains this invention in more detail below.
Example 1 (Ag15Zn10) (In15Sn10) (Sb10Te15) After producing the target for spatters which has composition of 2 and preparing the record layer of 1000A ** by the same method as examples 1 and 2 on a glass substrate with a diameter [of 130mm], and a thickness of 1.2mm, it was 1000A-thick-formed, having used the silicon nitride as the protective coat. And the optical property and heat characteristic of this record layer were first measured by the spectrophotometer and DSC as well as examples 1, 2, and 3 with the test piece. Reflection factor change was about 20% after vacuum evaporationo and initialization (amorphous) (crystalline substance) (lambda= 780nm). Moreover, permeability is about -15% and is larger than same independent ZnSnSb2 smaller about 20% than independent AgInTe2 and about 10%. Therefore, increase of the contrast by interference is attained with increase of an absorption efficiency. Moreover, the melting point was 490 degrees C and crystallization temperature was before and after -150 degrees C.
Next, the disk property of this record layer was measured like examples 1 and 2. Record, reproduction, and elimination were performed by irradiating the semiconductor laser light (lambda= 780nm) which extracted the beam diameter to 1 micrometerphi grade, rotating a record medium at the rate of 1800rpm first. In addition, record minimum power 8mW and 2mW elimination output of reproduction outputs of the record output were elimination minimum power 5mW. Moreover, it experimented in over-writing by 2 moreMHz after record by 3MHz of this output/elimination condition.
As a result, after 51dB of C/N ratio of initial record and over-writing was 49dB. On the other hand, the rate of elimination at this time was 30dB.
Moreover, although 10,000 records and the recurrence experiment of elimination were conducted, most falls of signal level were not accepted.
Example 2 (Zn15Cd10) Eight targets for spatters which have composition of Sn25 (Sb30P20) were produced, the record layer was formed by the same method as an example 1, and the property was

measured by the same method.
The melting point of this record layer was -510 degree C, and crystallization temperature was before and after -150 degrees C. Moreover, the reflection factor change during after initialization (result-izing) was it about 18% that it was amorphous (measurement wavelength of 780nm).
These values of changing by changing the composition ratio of Zn, Cd, Sb, and P are natural. This shows that the flexibility for achieving record sensitivity, elimination sensitivity, and the reinforcement of record according to the purpose is large. That is, improvement in sensitivity and contrast can be aimed at by combining well each properties (the melting point, the interference effect, etc.) of ZnSnSb2 and CdSnP2 compound which it has.
Next, rotating the record medium after initialization at the rate of 1800rpm, when the semiconductor laser light (oscillation wavelength of lambda= 780nm) which extracted the beam diameter to 1 micrometerphi grade irradiated, record, reproduction, and elimination were performed.
In addition, a record output is [2mW an elimination output, and the elimination minimum power of record minimum power 8mW and a reproduction output] 5mW. Moreover, 2M Hz performed the over-writing examination to the pan after record on this output/elimination condition.
Consequently, the C/N ratio of initial record hardly changed after over-writing with 50dB by 51dB. Moreover, it was checked that the rate of elimination at this time is 31dB, and it is a sufficiently usable stage although the elimination remainder is accepted a little. Moreover, although 10,000 records and the repetition experiment of elimination were conducted, most falls of signal level were not accepted but it was checked that a repetition property is also good.
Example 3 The target which has composition of Zn25 (In10Sn15) (Sb50) was produced, and the optical information record medium was produced by the same method as an example 1. a test piece -- an optical property and a heat characteristic -- respectively -- a spectrum -- it measured by the diameter of luminous intensity, and DSC Reflection factor change was about 18% after vacuum evaporationo and initialization (amorphous) (crystalline substance) (lambda= 780nm), the melting point was -430 degree C and crystallization temperature was before and after -135 degrees C. The feature of the record material used by this example is to aim at improvement in ** contrast to lower the melting point using ZnSnSb2 with the lowest melting point with a KARUKO pyrite compound, extend a band gap by the effect of a pan In, and use the interference effect.
Next, record, reproduction, and elimination were performed by irradiating the semiconductor laser light (lambda= 780) which extracted the beam diameter to 1 micrometerphi grade, rotating the record medium after initialization at the rate of 1800rpm. In addition, record minimum power 7mW, 2mW of reproduction outputs, and the elimination output minimum power of the record output were 5mW. Moreover, the over-writing experiment was conducted on the further after record by 2MHz on this output/elimination condition.
As a result, the C/N ratio of initial record showed the value also with after [as good] 52dB and over-writing as 50dB. Moreover, the rate of elimination at this time was 30dB.
Moreover, although 10,000 records and the repetition experiment of elimination were conducted, most falls of signal level were not accepted.
By using the record layer of this invention from the above example, it is clear that improvement of a property is repeatedly realizable for the improvement row of record sensitivity, elimination sensitivity, and the rate of elimination.
[Effect of the Invention]
The plural compounds of the aforementioned general formula used by this invention as explained above, The optical constant is begun by changing the composition element ratio, and when controlling arbitrarily a band gap, thermal conductivity, the specific heat, the melting point, a crystallizing point, and activation energy in the large range uses it as a record material for possible hatchet phase-change type optical memory, the improvement in record sensitivity and elimination sensitivity, improvement of elimination, and the reinforcement of record can be achieved.

[Translation done.]

PRIOR ART

[Description of the Prior Art]
The so-called phase-change type record medium which uses transition between a crystal-amorphous interphase or a crystal-crystal phase by irradiation of an electromagnetic wave, especially a laser beam as one of the optical-memory media in which informational record and reproduction, and elimination are possible is known well. Especially, by optical porcelain memory, since over-writing by the difficult single beam is possible and the optical system by the side of a drive is also more simple, the research and development are active recently. As the Institute of Electronics and Communication Engineers collected works CPM 87-90 and its typical example of material, the so-called charges of a chalcogen system alloy, such as germanium-Te, germanium-Te-Sb, germanium-Te-S, germanium-Se-S, germanium-Se-Sb, germanium-As-Se, In-Te, Se-Te, and Se-As, are mentioned as indicated by USP3,530,441. Moreover, the proposal of the material which added Au (JP,61-219692,A), Sn, Au (JP,61-270190,A), Pd (JP,62-19490,A), etc. in the germanium-Te system for the purpose of the improvement in stability, high-speed crystallization, etc., the proposal of material (JP,62-73438,A) which specified the composition ratio of germanium-Te-Se-Sd for the purpose of the improvement in repeatability ability of record/elimination are made.
However, the neither can say it as what may satisfy many properties of all demanded as a phase-change type rewritable optical-memory medium. It is the problem of the utmost importance which should be erased at the time of improvement in record sensitivity and elimination sensitivity, and over-writing, and the reinforcement of prevention of the elimination ratio fall by the remainder and the Records Department, and the non-Records Department should solve especially.

[Translation done.]